ARKIV FÖR FYSIK Band 14 nr 17

Communicated 4 June 1958 by G. Borelius and Folke Odqvist

Calorimetric measurements on the structural energy of an annealed metal of high purity

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With 10 figures in the text

Introduction

The structural disorder in pure undeformed metals due to point imperfections has been studied in the last few years in a number of resistometric investigations [1–6]. In the present research a series of measurements on the structural energy of silver have been made using an isothermal micro-calorimetric method. The range of accurate observations was experimentally restricted to some hundreds of degrees above room temperature. In this range it was found that increasing temperature leads to an isothermal absorption of energy, which becomes larger with increasing grain size and purity of the metal. In this paper the results of these measurements will be given and possible explanations discussed.

Method

Silver of 99.999 % purity (Johnson, Matthey & Co.) and of about 99.9 % purity has been used. The specimens consisted of small pieces of about centimeter size and of a total mass of approx. 0.5 mole. The metal was placed in thin-walled argon-filled pyrex containers, which were evacuated and sealed. A thermocouple was introduced in the centre of the container. By convenient heat treatment, sometimes in combination with plastic deformation, the mean grain size of the specimens was varied within certain limits.

The calorimetric apparatus for the temperature range 100° to 400°C was an electrically heated and regulated thermostat described earlier [7]. The temperature of the central part of it could be kept extremely constant. In this part of the thermostat a measuring cell was located, consisting of a differential arrangement of about thirty thermocouples by which it was possible to follow the temperature variations of the specimen relative to the temperature of the thermostat during the measurements. Owing to the very good stability of temperature of the thermostat, the difference in temperature could be followed down to some tenthousandths of a degree.

When a measurement at elevated temperatures was to be started the specimen was rapidly heated to the thermostat temperature in an external oven. By means of the thermocouple attached to the specimen, its temperature could be followed. When the specimen reached the same temperature as the thermostat it was intro-

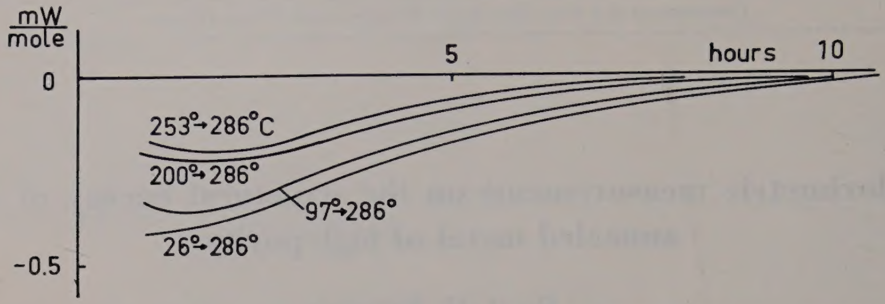

Fig. 1. Rate of energy absorption versus time for measurements on 99.9 % Ag at 286°C after annealing at varying temperatures.

duced into the measuring cell. Due to the enclosing of the metal in evacuated containers it took a certain time, half an hour or more, until the temperature of the specimen was entirely in equilibrium with that of the thermostat and accurate results were obtained. The readings gave the rate of change of energy as a function of time. Absolute values were obtained by calibrating with a known amount of Peltier heat released in the junction of the thermocouple of the specimen.

For measurements at room-temperature an arrangement of thermocouples similar to that mentioned above was enclosed in a copper container and placed in the center of a large water tank. The specimens could be introduced into the measuring cell by a vertical tube ending somewhat above the water surface. The tank was situated in a room, the temperature of which was kept constant within some hundredths of a degree. Because of the great heat capacity of the water volume, its temperature varied slowly, some tenthousanths of a degree per hour, which made measurements of good precision possible also in this case.

Measurements on 99.9 % silver

Some calorimetric series were first run on technically pure silver, having a grain size about 1 mm. Two types of pre-annealing of the specimens were tried. In one series we have kept the measuring temperature constant at 286°C. After some days annealing at this temperature the specimen was cooled in air to different lower temperatures, kept there for some days and then rapidly heated to the measuring temperature. This treatment gave rise to an isothermal absorption of heat in the specimen. With increasing difference in temperature the amount of energy absorbed increased (fig. 1). The rate of energy absorption follows an exponential time-law $dQ/dt = (dQ/dt)_0 e^{-t/\tau}$ except at the beginning of the measurements where disturbances from the introduction of the specimen into the thermostat still remain. In another series the measuring temperature was varied. After some time at this temperature the specimen was cooled down to room-temperature, and after some days heated to the measuring temperature again. Also in this case an absorption of heat increasing with the difference in temperature was obtained (fig. 2). As expected the two types of pre-treatment gave similar results. The energies obtained by integration of the measuring curves, exponentially extrapolated to zero time (table 1), have been plotted versus the temperature (fig. 3). The energies from fig. 1 have been laid in with the energy

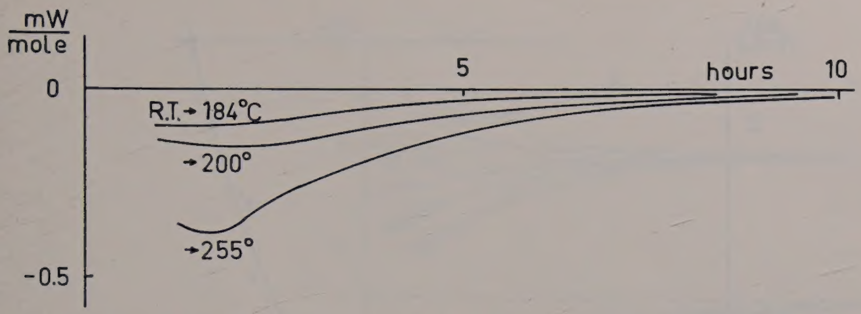

Fig. 2. Rate of energy absorption versus time for measurements on 99.9 % Ag at varying temperatures after aging at room-temperature.

of the constant measuring temperature (286°C) as a reference point, while those of fig. 2 have been plotted with the energy at room-temperature as a basis. The points, in both cases, describe on the whole a common curve.

As a check that no extraneous effects were obtained from the enclosing of the metal in the glass containers, some measurements have also been made on a specimen in the form of a massive silver cylinder, which was placed directly into the measuring cell. With similar pre-annealings and grain size as the glass-enclosed specimens, the results were similar as long as the measuring temperatures were below say 200°C. At higher temperatures, however, a small oxidation of the silver cylinder was obtained which disturbed the result. Although these measurements were carried out in an inert atmosphere it was not possible to avoid this oxidation effect. As a further check that a possible absorption of moisture or gases on the surface of the glass containers or the metal cylinder had no influence, some measurements were also made on empty glass containers pre-annealed in a similar way as the real specimens. No effect was, however, obtained from these dummies.

The described phenomena are not specific for silver. The same form of heat absorption has also been observed in other pure metals as copper, gold and aluminium, which were heat treated in a similar way as the silver specimens. Detailed measurements have, however, not yet been made on these metals.

Table 1.

T_a °C	T_m °C	τ h	$\left(\frac{dQ}{dt}\right)_0$ mW/mole	Q cal/mole
253	286	2.8	0.4	1.0
200	286	3.2	0.5	1.4
97	286	3.2	0.7	1.9
26	286	3.3	0.8	2.3
26	184	3.0	0.2	0.5
26	200	3.0	0.3	0.8
27	255	2.8	0.7	1.7

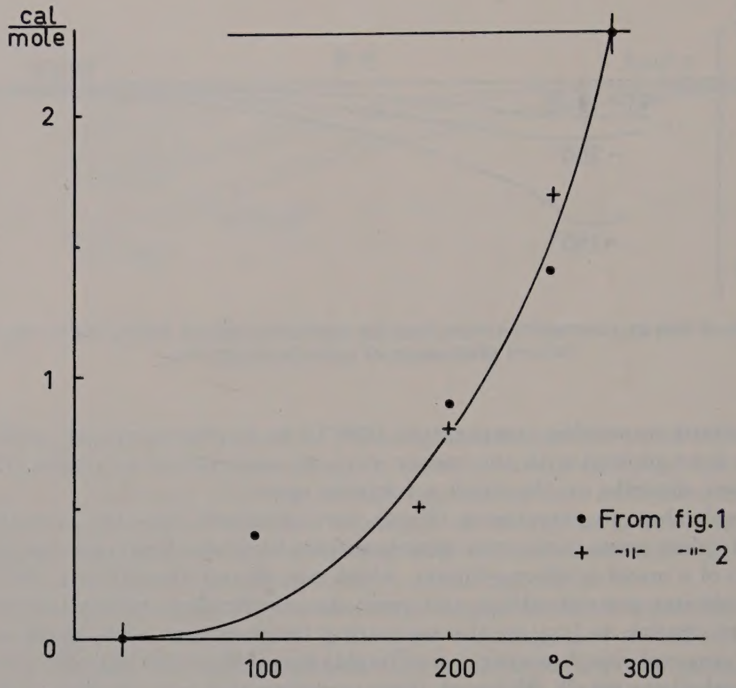

Fig. 3. Absorbed energy in 99.9 % Ag as a function of temperature. The zero point is arbitrary.

Measurements on 99.999 % silver

Most of the time has been devoted to measurements on the "spectrographically pure" material. Three specimens of different grain size have been used: A, with a grain size of about 0.3 mm, B, with grains of about 1 mm size, and C, which was almost monocrystalline.

In one series of measurements the specimens were annealed in essentially the same way as in the case giving the results in fig. 2. Hence the specimens were at first kept for some days at the measuring temperature in order to equilibrate the structure of the metal at this temperature and were then cooled down in air to room temperature. After two days they were again heated to the temperature of the thermostat and measured. The rate of change of energy versus time at different temperatures is shown for the three specimens in fig. 4. The rate of energy absorption has the same dependence on time as in figs. 1 and 2. The energies, Q, obtained by integration of the exponentially extrapolated measuring curves have been collected in table 2 as well as the time constants (τ) of the curves and the initial values of dQ/dt. T_a is the aging temperature and T_m the measuring temperature. Due to somewhat reduced sensitivity of the thermostat the results at 370°C are less accurate than those of the lower temperatures.

The time of aging at room-temperature seems not to be very critical. The same amount of energy was taken up when the specimens were measured after they had just reached room-temperature as in the case that they were aged for some days at this

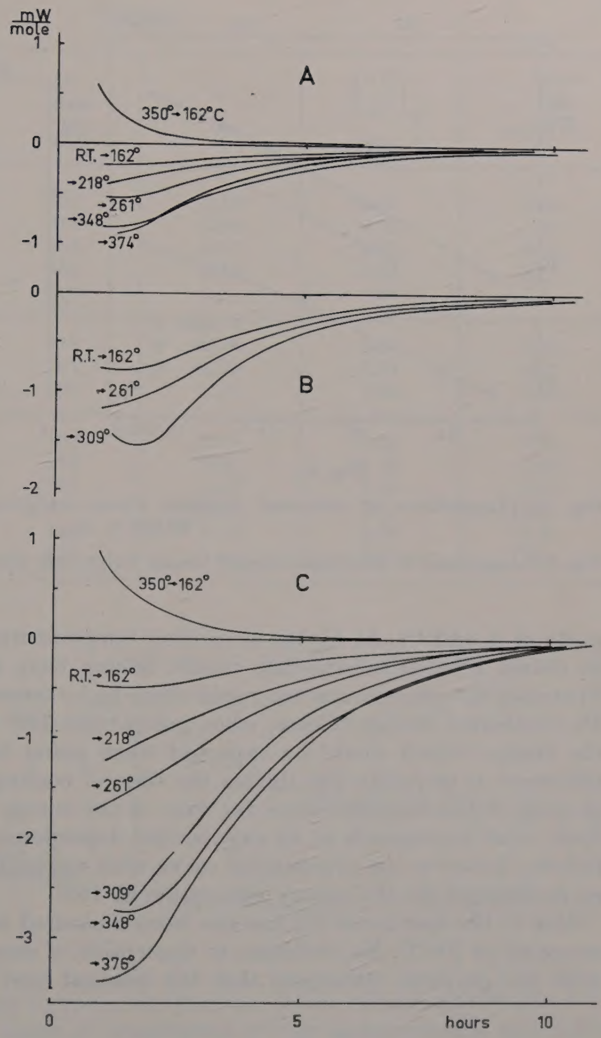

Fig. 4. Rate of energy absorption and release versus time for measurements on 99.999 % Ag after different pre-annealings.

temperature before being measured. Already after cooling to room-temperature the specimens seem to have reached a state very near to their final state at this temperature. A contributory cause of this state of matter may be that due to the enclosing of the metal in evacuated glass tubes it takes rather long time, 15 to 20 minutes, for the specimens to cool down to room-temperature. Although the cooling time can be reduced for the massive cylinder specimens it seems not to be possible to quench in the effect in any case on account of the relatively large mass necessary for calorimetric measurements of the actual type.

In some cases the specimens were pre-annealed at a higher temperature than that of the thermostat and then cooled down to this temperature and measured. At about 160°C a continuously decreasing evolution of heat was observed (the upper

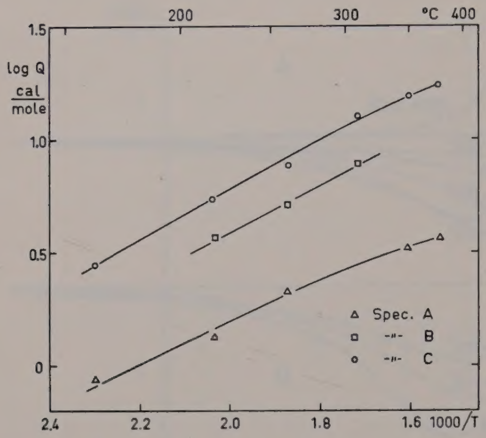

Fig. 5.

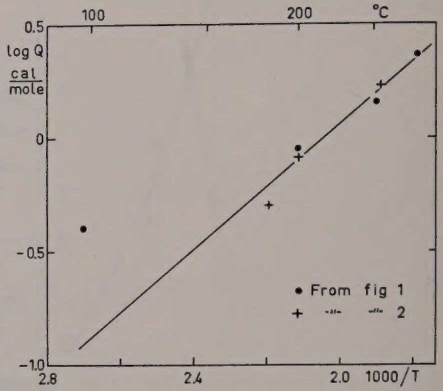

Fig. 6.

Fig. 5. Logarithms of absorbed energies versus reciprocals of absolute temperatures for 99.999 % Ag.

Fig. 6. Logarithms of absorbed energies versus reciprocals of absolute temperatures for 99.9 % Ag.

parts of A and C). At higher measuring temperatures it was, however, not possible to obtain reliable calorimetric results arising from a heat treatment of this kind. Probably the process was too rapid there to be measured with the present method. The measured energy release, when going from 350° to 162°C is only about 20 % of the energy which would be expected when going from 162 to 350°C. The energy difference is probably lost during the time of cooling from 350° to 162°. In the beginning of the measurements the rate of the energy release decreases more rapidly than what corresponds to an exponential dependence on time. The tail of the effect follows, however, an exponential curve with approximately the same time constant as is obtained for the energy absorption at 162°.

One of the specimens (C) has also been measured at room-temperature after being annealed at 250°C. No evolution or absorption of energy was observed, in agreement with the previous statement that the residual heat is small at room-temperature.

The dependence on temperature

The absorbed energies have been plotted logarithmically versus the reciprocal temperature in fig. 5 for the high-purity specimens A, B and C and in fig. 6 for the specimens of technically pure silver. For samples A and C where the measurements have been extended to somewhat higher temperatures the change of energy with temperature seems to decrease thus tending to make the lines joining the points in the diagram somewhat concave downwards. The slopes of the lines in fig. 5 correspond to an average energy of formation for the process of about 4700 cal/mole within an accuracy of about 15 per cent. The energy may be somewhat lower at higher temperatures due to the concavity mentioned. From fig. 6 an energy of formation of about 6000 cal/mole was obtained for the less pure silver. The limit of error is, however, larger in this case.

Table 2.

	T_a °C	T_m °C	τ h	$\left(\frac{dQ}{dt}\right)_0$ mW/mole	Q cal/mole
A	27	162	3.13	0.32	0.86
	27	218	2.80	0.55	1.33
	27	261	2.35	1.05	2.12
	27	348	2.45	1.55	3.27
	27	374	2.2	1.9	3.6
B	26	218	2.76	1.54	3.66
	27	261	2.37	2.51	5.12
	27	309	2.07	4.32	7.69
C	27	162	3.60	0.92	2.85
	26	218	3.37	1.89	5.48
	27	261	2.62	3.39	7.64
	26	309	2.52	5.80	12.57
	27	348	2.73	6.60	15.50
	27	376	2.4	8.3	17.1

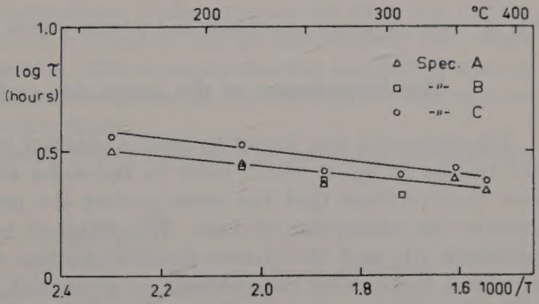

Fig. 7. Logarithms of time constants versus reciprocals of absolute temperatures for 99.999 % Ag.

An extrapolation of the lines to room temperature gives values of Q of about 0.1 cal/mole which is within the limits of uncertainty of our measurements and makes the negative results of aging or measurements at room temperature understandable. The curve in fig. 3 has been drawn in conformity with this exponential extrapolation.

As was pointed out previously, the rate of energy absorption decreases exponentially with time. The time constants of the curves, given in table 2, have been introduced in fig. 7 in a logarithmic scale as a function of the reciprocal temperature. The influence of temperature on these values is weak. The mean energy of activation obtained from the slope of the lines is of the order 1000 cal/mole.

Due to the complex form of the curves for the energy release after lowering of the temperature it has not been possible to determine the dependence on temperature of this process.

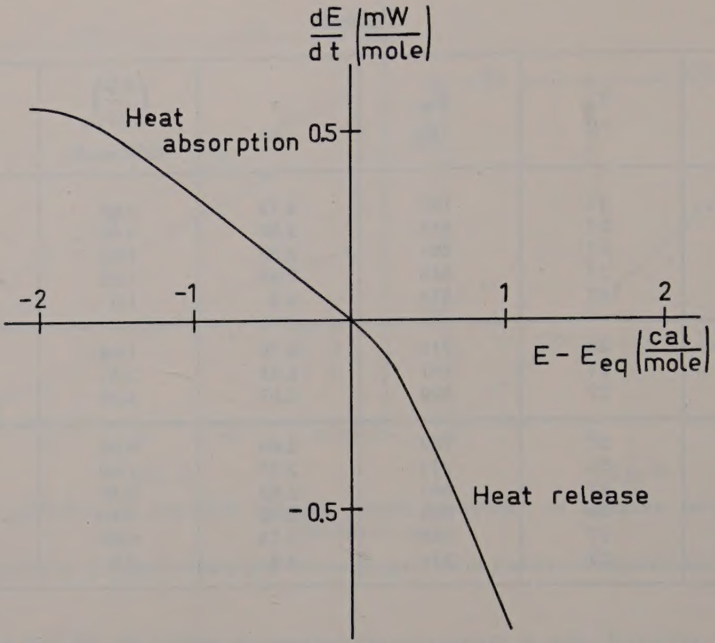

Fig. 8. Rate of energy absorption and release versus relative energy for specimen C at 162°C.

The dependence on the grain size and the purity of the material

The grain size was found to have a marked influence on the studied effects. From the results in fig. 5 which refer to the same material (99.999 %) but varying grain size it is obvious that the more perfect the material, i.e. the larger the grains, the greater the absorption of heat. The distance between the lines for the fine-grained specimen (A) and the almost monocrystalline specimen (C) corresponds to a factor of about three. This dependence on grain size may explain why these effects were not observed in earlier measurements on a cold-worked pure metal [8] or on grain growth in pure metals [7], where the grain sizes were smaller than in the present case.[1]

The influence of impurities has not been investigated to any great extent. By comparing the results of the 99.9 % specimen with specimen B of the 99.999 % material which have about the same grain size, some information about this topic may be obtained. It is then found (cf. figs. 5 and 6) that the absorbed energy is about four times as large for the purest material as for the other. The energies of formation are, however, about the same for both materials.

The kinetics of the measurements

One type of representation of the present results which has several advantages, is the dE/dt versus E diagram where E is the internal energy of the metal. Fig. 8 shows dE/dt for the absorption and release of energy at 162°C in the almost monocrystalline specimen as a function of $E - E_{eq}$. The former case corresponds here to $dE/dt > 0$

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[1] Possibly a small effect could be observed in [7].

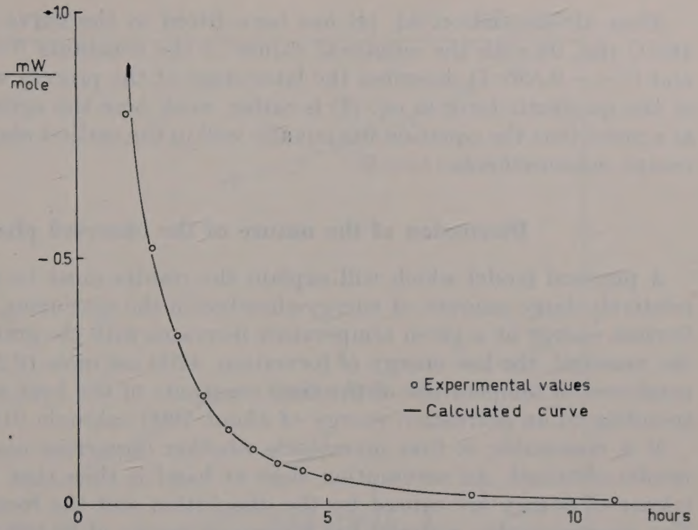

Fig. 9. Rate of energy release versus time for specimen C measured at 162°C.

and the heat release in the specimen to $dE/dt < 0$. E_{eq} denotes the equilibrium value of the energy of the specimen at the measuring temperature. For $E - E_{eq} < 0$ there is a linear relationship in fig. 8 as a consequence of the exponential time law for the measurements. When $E - E_{eq} > 0$, dE/dt is found to change more rapidly than what corresponds to an exponential time relation. The negative and the positive branch of the curve in fig. 8 are, however, continuous, expressing reversibility for the process in a small region around the equilibrium point.

From fig. 8 it is obvious that the absorption of heat may be described phenomenologically by an expression like

$$\frac{dE}{dt} = -\alpha (E - E_{eq}) \tag{1}$$

or in integrated form

$$E = E_{eq} - \Delta E \cdot e^{-\alpha t}, \tag{2}$$

where ΔE is the difference between the equilibrium energy E_{eq} and the energy E_a at the aging temperature and α depends on temperature, grain size and the purity of the metal.

For $E - E_{eq} > 0$ an analysis of the curve shows that the heat release may be considered to be built up of a linear relation as in eq. (1) and a quadratic function of E and thus can be written in the following form

$$\frac{dE}{dt} = \beta (E - E_{eq}) + \gamma (E - E_{eq})^2 \tag{3}$$

or integrated

$$E = E_{eq} - \frac{\beta}{\gamma - C \cdot e^{-\beta t}}, \tag{4}$$

where β and γ may depend on the same factors as α. The constant C is given from the boundary conditions $t = 0$; $E = E_a$.

After differentiation eq. (4) has been fitted to the curve for the heat release at 162°C (fig. 9) with the empirical values of the constants $\beta = -0.345$; $\gamma = -0.520$; and $C = -0.580$. It describes the later stage of the process well but as the influence of the quadratic term in eq. (3) is rather weak here the agreement cannot be taken as a proof that the equation fits equally well in the earliest stages of the process which escape measurements.

Discussion of the nature of the observed phenomena

A physical model which will explain the results must be able to account for the relatively large amount of energy absorbed in the specimens, the fact that the equilibrium energy at a given temperature increases with the grain size and the purity of the material, the low energy of formation, 4700 cal/mole (0.2 eV), and the weak dependence on temperature of the time constants of the heat-absorption curves corresponding to an activation energy of about 1000 cal/mole (0.04 eV).

It is reasonable to first investigate whether impurities can be responsible for the results obtained. An assumption close at hand is then that the absorption and the release of energy are caused by the dissolution and the formation of a precipitate. The spectrographic material has a nominal purity of 99.999 %. Silver has, however, a certain solubility of oxygen which escapes this analysis. At 400°C the amount of oxygen in solution is about 10^{-3} wt % [9]. Including this oxygen content the complete precipitation of the impurities thinkable would with an average heat of solution of 5000 cal/mole correspond to an energy of some tenths of a cal/mole while the observed effects are of the order some calories per mole. Further the influence of the grain size and the impurities also contradicts the impurity hypothesis.

A second model which would also correspond to an absorption of energy with increasing temperature is the formation of thermal vacancies in the lattice and the appearance of jogs in the dislocation lines. For copper and gold, resistivity measurements have given an energy of formation of vacancies of about 1 eV [1, 4, 5]. No measurements have been reported for silver but it seems reasonable to expect a value of the same magnitude also in this case. The energy of formation of the present effect corresponds, however, only to about 0.2 eV. The density of vacancies, estimated from the resistivity measurements, is also much too low in the temperature range of the present investigation to account for the energy absorption in the specimens. For Frenkel-defects, that is dissociated pairs of vacancies and interstitials, the situation is energetically still more unfavourable. The relatively large absorption of energy and the low energy of formation for the process also disagrees with the assumption that the measurements are caused by a change of the number of jogs in the dislocations.

The fact that impurities, vacancies, and dislocations interact introduces a third possibility. The absorption of energy in the specimens would in this case be caused by the decrease in density of the atmospheres of impurity atoms and vacancies surrounding the dislocations which occurs with increasing temperature. The mean energy of interaction between point imperfections and dislocations can be considered to be of about the same magnitude as the present energy of formation [10]. There are, however, other important facts contradicting this model. Due to the same reasons as above, the concentration of impurities and vacancies is not high enough to account for the energies absorbed. The dependence of the grain size and the purity of the material contradict also this explanation.

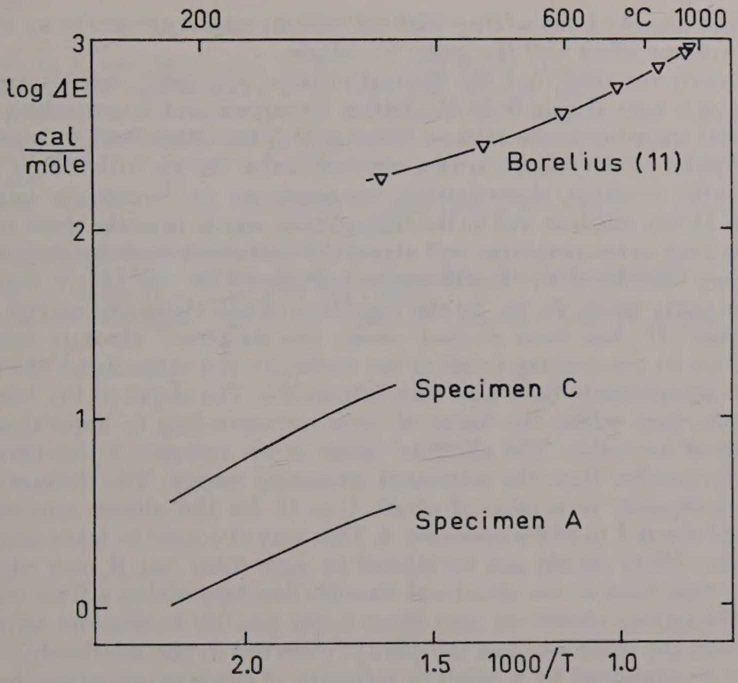

Fig. 10. Logarithms of change of structural energy versus reciprocals of absolute temperatures from measurements on 99.999 % Ag and estimated from [11].

Although one or more of the mechanisms postulated here may influence the calorimetric results it seems impossible that they can account for more than a small portion of the energies observed. As it seems unlikely that the remaining part of the effect should be caused by extraneous effects due to the method of the measurements, we are led to assume that there exists some energy-rich thermal disturbancy in the lattice of other type than those already considered. These disturbancies may either be restricted to the grain boundaries, or be a pure volume effect, or may be some interrelation between a volume effect and the grain boundaries. The first of these possibilities seems, however, to be excluded by the fact that the energy absorption increases with the grain size, that is with decreasing total grain-boundary area. As regards the volume effect it may be expected that this process corresponds to generation of some irregularity in the lattice and its annihilation by association. The effect may then be described by a differential equation of the following form

$$\frac{dE}{dt} = A - B \cdot E^n, \quad n = 1, 2, 3 \ldots, \tag{5}$$

where A expresses a constant rate of generation, and B may be considered as a recombination constant. The value of n depends on the complexity of the process. For association in pairs n is equal to 2. With $n = 1$ eq. (5) agrees with eq. (1). The existence of a pure volume effect in our case is, however, less probable on account of the marked influence of the grain size on the measurements. We therefore may assume with a certain degree of probability that the present results are due to an interaction between a volume effect and the grain boundaries.

It is currently assumed that the thermal increase of energy, entropy and volume is made up of a part arising from the lattice vibrations and a part which is due to the structural disorder in the lattice. Borelius [11] has attempted to represent the vibrational parts of the energy in face-centered cubic metals with Debye functions associated with constant characteristic temperatures. It is perhaps questionable whether the Debye function will be the fully correct way to describe these vibrational parts but as long as temperatures well above the characteristic temperature ($\theta = 215$ for silver) are considered the incorrectness introduced by the Debye function will probably be fairly small. In fig. 10 the logarithm of the structural energy for silver obtained from [11] has been plotted versus the reciprocal absolute temperature from 338°C up to the melting point of the metal. In the same figure the results of the present meaurements have also been introduced. The slopes of the lines are the same in both cases within the limits of error corresponding to approximately the same energy of formation. The absolute values of the energies of this investigation are, however, smaller than the estimated structural energy. The distance between the lines corresponds to a ratio of about 1 to 15 for the almost monocrystalline specimen and about 1 to 50 for specimen A. This may of course be taken as an indication that the effects should not be related to each other but it may also depend on the fact that most of the structural disorder develops within a time comparable to that of the atomic vibrations, and hence is not possible to measure anyhow. The dependence on the grain size and the purity, observed in the calorimetric measurements, may be explained by a catalytic influence of these imperfections by which a larger part of the effect is shifted towards shorter times and thus escapes measurements. In the present state of things it is not possible to say anything about the mechanism causing the structural energy.

Although the above model is of a speculative character it seems at present to represent a possible way to explain the calorimetric results obtained. There are, however, many open questions which we hope to be able to answer by further experimental work. Resistometric measurements as well as calorimetric studies of other pure metals are planned.

SUMMARY

Changes in the structural energy of well-annealed pure silver have been studied with a microcalorimetric method. Within a range of some hundreds of degrees above room-temperature it was found that increasing temperature gives rise to an isothermal absorption of energy in the metal which becomes larger with increasing grain size and purity of the metal. The temperature dependence of the amount of energy absorbed gives an average energy of formation of the process of 4700 cal/mole. The kinetics of the measurements gives an activation energy of about 1000 cal/mole. Different models for the explanation of the results are discussed.

ACKNOWLEDGEMENTS

I want to express my gratitude to Professor G. Borelius for valuable discussions and advice and the constant interest he has shown in my work. My thanks are also due to Mr. L. E. Larsson for good technical asistance. The financial costs of this work were covered by the Swedish Council for Technical Research.

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Tryckt den 19 september 1958

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